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*METHODS FOR THE ANALYSIS OF ILMENITE,  
TITANIUM-BEARING SLAGS AND  
OTHER ELECTRIC FURNACE SLAGS  
PART IVB: THE DETERMINATION OF  
ALUMINUM IN OTHER TYPES OF  
ORES AND SLAGS*

A. HITCHEN AND G. ZECHANOWITSCH

EXTRACTION METALLURGY DIVISION

JULY 1973

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METHODS FOR THE ANALYSIS OF ILMENITE, TITANIUM-BEARING  
SLAGS AND OTHER ELECTRIC FURNACE SLAGS

PART IVB: THE DETERMINATION OF ALUMINUM IN  
OTHER TYPES OF ORES AND SLAGS

by

A. Hitchen\* and G. Zechanowitsch\*\*

ABSTRACT

Adaptation of the method described in the previous report in this series\*\*\* to the determination of aluminum in a wide variety of ores and slags of quite different composition is described. Compatible methods for dissolution of these materials are also given.

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\*\*\* Part IVA

Direction des mines  
Bulletin technique TB 169

DES MÉTHODES POUR L'ANALYSE DE L'ILMÉNITE DES  
SCORIES TITANIFÈRES ET D'AUTRES SCORIES PROVENANT  
DU FOUR ÉLECTRIQUE

IV<sup>e</sup> Partie B - LA DÉTERMINATION DE L'ALUMINIUM DANS  
D'AUTRES TYPES DE MINÉRAIS ET DE SCORIES

par

A. Hitchen\* et G. Zechanowitsch\*\*

RÉSUMÉ

Les auteurs décrivent l'adaptation de la méthode décrite dans le rapport précédent de cette série\*\*\* pour la détermination de l'aluminium dans une grande variété de minerais et de scories de composition assez différente. Ils présentent aussi des méthodes compatibles pour la dissolution de ces matériaux.

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\*\*\*Partie IVA

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## INTRODUCTION

The analytical method used for the determination of aluminum in ilmenite and titaniferous slags was developed primarily for those materials but it was subsequently applied to chromite, vanadium-bearing coke fly ash and slags, uranium ores, tin ores, manganese ores and slags, and various minerals. The original method was modified to deal with chromium, vanadium, uranium, rare earths, tin, arsenic, and manganese, etc. that were present in these various other materials.

The methods used for the dissolution and treatment of these ores, slags, and minerals together with the results obtained are outlined in the following sections.

### A. Chromium Ores and Vanadium-Bearing Coke Fly Ash and Slags

The determination of aluminum was required in chromite and in vanadium-bearing coke fly ash and slags being investigated at the Mines Branch.

The method for the analysis of ilmenite ores and slags described in the previous report in this series<sup>(1)</sup> appeared to be generally applicable. It was shown in Table 7 that large amounts of chromate do not interfere with the titration of aluminum and that the interference of vanadium can be prevented by adding hydrogen peroxide to the solution. The presence of other potential interferents such as nickel made it desirable to include the extraction step. In addition, an ammonium hydroxide precipitation was considered necessary to remove the bulk of the chromate and/or vanadate before extraction in order to decrease the number

of sodium diethyldithiocarbamate (DEDTC) and chloroform extractions that would be required to remove these impurities. The ammonia separation also serves to eliminate the large amounts of sodium salts arising from the sodium peroxide fusion and the washings.

The method that was developed is described below.

Method for Chromite Ores and Vanadium-Bearing Coke Fly Ash and Slags

1. Dissolution of Sample and Preliminary Precipitation of Aluminum with Ammonium Hydroxide

Fuse a 0.1 to 0.5-gram sample with 1 to 6 grams of sodium peroxide plus 5 to 6 pellets of sodium hydroxide in an iron or zirconium crucible until decomposition is complete. This may take 5 to 10 minutes or longer depending on the refractoriness of the particular sample. Cool, transfer the sample and crucible to a Teflon beaker, and leach with 50 to 100 ml of water. Remove and rinse the crucible with a little dilute hydrochloric acid to dissolve any precipitate or residue, adding the rinsings to the beaker. From this point, either of two procedures may be followed, depending on whether iron or zirconium crucibles have been used for the fusion.

(a) If zirconium crucibles have been used, boil the solution in the Teflon beaker to decompose the peroxide. Filter off the iron and zirconium hydrous oxides and wash the precipitate with hot 5 % sodium hydroxide solution, combining the wash solution with the filtrate. Redissolve the precipitate in hot dilute hydrochloric acid and reprecipitate the iron and zirconium with sodium hydroxide solution. Filter and wash as before and combine the filtrates. Discard the precipitate of iron and zirconium



oxides. If higher accuracy is desired, however, reprecipitate a third time.

Acidify the filtrate slightly with sulphuric or hydrochloric acid, bring the solution to boiling, add methyl red indicator, and precipitate the aluminum by carefully adding ammonium hydroxide until the methyl red changes from red to yellow and then 2 to 3 drops more.

Boil the solution for a few minutes to coagulate the precipitate, filter, and wash the impure precipitate a few times with hot 2 % ammonium chloride wash solution that has previously been adjusted to the methyl red end-point with ammonium hydroxide. Transfer the filter paper and precipitate to a beaker and destroy the paper by treating it with 20 ml of concentrated nitric acid and 2 to 5 ml of 72 % perchloric acid and evaporate to fumes of perchloric acid. Dissolve the residue in a small amount of hydrochloric or perchloric acid, dilute to volume in a volumetric flask and take suitable aliquots for the extraction. If only a small amount (5 to 20 mg) of aluminum is present, the whole sample may be taken through the extraction step.

(b) If iron crucibles have been used for the fusion, boil the solution to decompose the peroxide and acidify with dilute sulphuric or hydrochloric acid. Add methyl red indicator and precipitate the aluminum and iron with ammonium hydroxide as described above in (a). If much iron is present, the methyl red colour will be masked, so adjust the pH to 6 to 7 with the aid of pH test paper. Boil to coagulate the precipitate, filter, and wash. Complete as described in (a).

## 2. Extraction Step and Titration of Aluminum

From either the whole residue or a suitable aliquot of the sample solution, obtained from either procedure (a) or (b), extract the remaining impurities and titrate the aluminum according to the procedure described in the previous report in this series (Reference 1, page 8). Several chrome ores and vanadium-bearing coke fly ash samples and slags were analyzed by the above procedures and the results are shown in Table 1.

The percentage of aluminum found in the B.C.S. Standard Grecian Chrome Ore by the proposed method agrees well with the certified value and falls within the range of aluminum values as determined by other standard methods. No comparison values were available for the other chrome ores and for the coke fly ash but, on the basis of the work reported on the analysis of titanium-ferrous ores and slags<sup>(1)</sup>, there is no reason to believe they are inaccurate. To illustrate the complexity of these materials, their composition is given in Table 2.

### B. Uranium Ores

For the determination of aluminum in uranium ores, the general method had to be modified to take uranium and, in some ores, rare earths into account.

Two methods of dissolution were investigated. The first was a multi-acid treatment, and the second was a sodium peroxide fusion. These procedures are described below\*.

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\*If only a little carboniferous material is present, it will likely be destroyed by either the nitric and perchloric acids or by the sodium peroxide fusion. If much is present, a preliminary ignition may be required to remove it before proceeding with either the multi-acid treatment or the sodium peroxide fusion. No specific directions can be given because a great deal depends on the particular samples.

TABLE 1

Determination of Aluminum in Chrome Ores and Vanadium-  
Bearing Coke Fly Ash and Slags

| Sample No. | Description                                 | % Al      |             |              |
|------------|---|-----------|-------------|--------------|
|            |   | Range     | Cert. Value | Found*       |
| BCS 308    | B.C.S. Standard Grecian<br>Chrome Ore # 308 | 10.0-10.4 | 10.3        | 10.00, 10.22 |
| EMP 2856   | Bird River Chromite                         | -         | -           | 14.20, 14.26 |
| EMQ 188    | Sintered Chrome Ore                         | -         | -           | 7.63, 7.60   |
| EMP 3016   | Bird River Chromite                         | -         | -           | 8.86, 8.85   |
| EMP 3437   | Coke Fly Ash                                | -         | -           | 1.63, 1.64   |
| EMQ 739    | Coke Fly Ash Slag                           | -         | -           | 2.12, 2.06   |
| EMQ 740    | Coke Fly Ash Slag                           | -         | -           | 1.91, 1.88   |

\* On duplicate weighed samples

TABLE 2

General Composition of Samples Analyzed by the Proposed Method

| Sample No, | Material            | Cr   | V    | Total Fe | Si   | Ca   | Mg   | C    | Ni   | Cu   | Total S | P     | Mn    | Ti   |
|------------|---------------------|------|------|----------|------|------|------|------|------|------|---------|-------|-------|------|
| BCS 308    | Chrome Ore          | 28.4 |      | 11.8     |      | 0.25 | 10.0 |      |      |      |         |       | 20.12 | 20.1 |
| EMP 2856   | Chromite            | 23.8 |      | 11.5     | 1.06 | 0.17 | 10.6 |      |      |      |         |       |       |      |
| EMP 188    | Sintered Chrome Ore | 27.4 |      | 20.2     | 2.69 | 4.76 | 6.25 | 0.66 |      |      | <0.01   | <0.01 |       |      |
| EMP 3016   | Chromite            | 28.5 |      | 19.3     | 2.00 | 0.25 | 5.30 |      |      |      |         |       |       |      |
| EMP 3437   | Coke Fly Ash        |      | 17.6 | 9.3      | 4.95 | 0.62 | 0.52 | 3.66 | 11.6 |      | 3.24    |       |       |      |
| EMP 739    | Coke Fly Ash Slag   |      | 20.0 | 16.1     | 13.5 |      | 4.23 |      | 0.75 | 0.04 | 1.10    |       |       |      |
| EMP 740    | Coke Fly Ash Slag   |      | 19.1 | 16.3     | 13.0 | 0.73 | 3.83 |      | 3.04 | 0.09 | 1.81    |       |       |      |

Method (1) Multi-Acid Dissolution

Treat a 0.2 to 1-g sample of the ore in a Teflon beaker with 10 to 15 ml of 16 M nitric acid, 5 to 10 ml of 48 % hydrofluoric acid, and 10 ml of 72 % perchloric acid. Evaporate the solution to fumes of perchloric acid, add more nitric and hydrofluoric acids, if necessary, and fume again. Rinse down the sides of the beaker with water and evaporate to fumes again. Repeat to ensure the removal of fluoride. Dissolve the sample in water and dilute to about 100 ml\*.

Bring the solution to a boil and carefully add a solution of sodium hydroxide until a faint precipitate of hydrous iron oxide appears. Add a few drops of hydrochloric acid to clear the solution. Pour the solution carefully into 100 ml of a boiling solution of 10 % sodium hydroxide in a Teflon beaker and digest the solution for a few minutes to coagulate the precipitate. Filter the solution through Whatman No. 541 or No. 52 paper and wash the precipitate with hot 5 % sodium hydroxide wash solution. Collect the filtrates in a Teflon beaker to avoid pick-up of aluminum from a glass beaker. If considerable iron and rare earths are present, or if a higher accuracy is desirable, dissolve the precipitate in hydrochloric acid and precipitate the iron and rare earths again with sodium hydroxide. Acidify the filtrate with either sulphuric or hydrochloric acid, bring to a boil, add methyl red indicator, and then carefully add a solution of 1.5 M ammonium hydroxide containing 10 % w/v of ammonium carbonate until the methyl red colour changes to yellow and add 2 to 3 drops more. Digest a short time to

---

\* If necessary, dilute to volume in a volumetric flask and take aliquots sufficient to contain 10 to 20 mg of aluminum, otherwise, proceed using the whole sample.

coagulate the precipitate. Filter and wash the impure aluminum hydroxide precipitate with hot 2 % ammonium chloride solution that has previously been adjusted to the methyl red end-point with ammonium hydroxide. Transfer the paper and precipitate to a beaker, destroy the paper by treatment with 20 ml of concentrated nitric acid and evaporate to fumes after adding 2 to 5 ml of 72 % perchloric acid. Dilute to 100 ml with water, add 5 ml of glacial acetic acid and 15 ml of 25 % sodium acetate solution, and adjust the pH to 2 with either hydrochloric acid or sodium hydroxide. Extract to remove the remaining impurities and titrate the aluminum according to procedure described previously (Reference 1, page 8).

#### Method (2) Sodium Peroxide Fusion

Fuse 0.2 grams of sample with 1 to 1.5 gram of sodium peroxide in an iron, or zirconium, crucible. Leach the slag with about 100 ml of water in a Teflon beaker. Rinse the crucible with a little hydrochloric acid and add the rinsings to the sample in the beaker. Boil the solution to decompose the peroxide, and filter, collecting the filtrate in a clean Teflon beaker. Wash the precipitate with hot 5 % sodium hydroxide solution. Dissolve the precipitate in hot dilute (10 to 20 %) hydrochloric acid and precipitate the iron and rare earths again with hot sodium hydroxide solution. Filter and wash the precipitate with hot 5 % sodium hydroxide solution. Acidify the filtrate with sulphuric or hydrochloric acid, precipitate the aluminum with

ammonium hydroxide + ammonium carbonate solution, and finish the determination as described in Method (1) above\*.

Several uranium ores were analyzed by each of the above procedures, and the results are shown in Table 3.

TABLE 3  
THE DETERMINATION OF ALUMINUM IN URANIUM ORES

| Sample   | Sample            | Method Followed | % Al <sub>2</sub> O <sub>3</sub> Found | Average |
|----------|-------------------|-----------------|--|---------|
| EMQ 2030 | Denison Feed      | 1               | 4.34, 4.34                             | 4.34    |
| EMQ 2030 | Denison Feed      | 2               | 4.49, 4.47                             | 4.48    |
| EMQ 2035 | Denison Low-Grade | 1               | 8.60, 9.08                             | 8.84    |
| EMQ 2035 | Denison Low-Grade | 2               | 9.18, 8.88                             | 9.03    |
| EMQ 3012 | Beaverlodge No. 1 | 1               | 12.81, 12.41                           | 12.61   |
| EMQ 3012 | Beaverlodge No. 1 | 2               | 13.34, 13.39                           | 13.37   |

The results in Table 3 indicate that Method (1) using the multi-acid treatment tends to give slightly lower values than Method (2), and the precision is generally not as good.

\* In Method (2) silica is not removed entirely and, after the filter paper has been destroyed with nitric and perchloric acids, it is precipitated and dehydrated. If the amount of silica is considerable it may entrain small amounts of aluminum. Therefore, filter it off, ignite it in a platinum crucible, and treat the residue with sulphuric and hydrofluoric acids to volatilize the silica. Fuse the residue with a little sodium bisulphate, or pyrosulphate, and finally combine the melt with the original filtrate. If only a few milligrams of silica are observed it may generally be ignored and extracted without being removed.

This is attributed to the fact that inadvertently only one precipitation with sodium hydroxide was done in Method (1) instead of two as in Method (2). Moreover, it is possible that the fluoride was not completely removed in spite of repeated fuming of the sample. However, bearing these facts in mind, the results are not grossly at variance and Method (1) is probably capable of yielding the same results as Method (2) if a double sodium hydroxide precipitation is made.

Because Method (1) is slower and because of the necessity of and the inherent uncertainty in removing all the fluoride, Method (2) is recommended. If large amounts of silica are present, however, it may be necessary to employ Method (1) or to remove the silica as described in the footnote to Method (2), page 9.

The Denison uranium ore contains rare earths which are not completely removed by ammonia precipitation, nor by diethyl-dithiocarbamate extraction. They cause erratic titrations and unsatisfactory end-points in the DCYTA titrations. The inclusion of the sodium hydroxide separation successfully eliminates them. If rare earths are known to be absent from the samples this step may be omitted and only the ammonium hydroxide + ammonium carbonate precipitation need be carried out. For large amounts of iron and uranium, double precipitation may be required to remove all the uranium.

C. The Determination of Aluminum in Tin-Bearing Ores and Concentrates

The ores and concentrates to be analyzed for aluminum were very complex and were from New Brunswick (Table 4). The



TABLE 4 .

Typical Analysis of New Brunswick Tin Ores  
and Concentrates

|                  | As Conc. | Cu Conc. | Bulk Conc. | Ore* |
|------------------|----------|----------|------------|------|
| Cu               | 0.2%     | 15%      | 1%         | 2%   |
| Pb               | 0.3      | 2        | 1          | 2    |
| Zn               | 1        | 20       | 3          | 17   |
| Bi               | 1        | 1        | 0.5        | <0.1 |
| Mo               | 0.5      | 0.2      | 0.5        | <0.1 |
| As               | 30       |          | 15         | 1    |
| Sb               | 1        | 0.1      | 1          |      |
| S                | 20       | 5        | 0.5        | 12   |
| SiO <sub>2</sub> | 5        | 10       |            |      |
| Fe               | 2        | 2        | 5          | 5    |
| Al               | 2        | 2        |            |      |
| In               | 0.2      | 1        | 0.2        | 0.1  |
| W                | 0.2      | 1        | 2          | <0.1 |
| Sn               |          | 5        | 1          | 2    |
| Ag               |          | 4        | 0.01       | 0.01 |
| F                |          |          | 30         | 5    |
| Ca               |          |          |            | 4    |
| Mg               |          |          |            | <0.1 |
| Ti               |          |          |            | <0.1 |
| Mn               |          |          |            | <0.1 |

The minerals in the ore were determined by X-ray diffraction, chemical analysis, and microscope as follows\*:

|              |       |              |       |             |       |
|--------------|-------|--------------|-------|-------------|-------|
| Quartz       | 34.7% | Sphalerite   | 25.1% | Molybdenite | 0.02% |
| Fluorite     | 6.6   | Stannite     | 2.9   | Wolframite  | 0.04  |
| Kaolinite    | 5.8   | Cassiterite  | 2.0   | Rutile      | 0.05  |
| Topaz        | 6.1   | Galena       | 2.0   | Bismuth     | 0.03  |
| Feldspar     | 0.8   | Pyrite       | 1.3   |             |       |
| Chlorite     | 7.0   | Arsenopyrite | 1.7   |             |       |
| Chalcopyrite | 3.8   |              |       |             |       |

\*Reference 2

general method developed for the titaniferous ores and slags, therefore, had to be modified to cope with the substantial amounts of tin, arsenic, lead, copper, zinc, etc., as well as the significant amounts of bismuth, molybdenum, indium, tungsten, silver, antimony, iron, and fluoride that were present.

1. Decomposition of Sample and Removal of Tin, Arsenic, Antimony, Silica, and Fluoride

Fuse a 0.5 to 1-gram sample with 5 to 10 grams of sodium peroxide plus 5 to 6 pellets of sodium hydroxide in an iron crucible. Cool, leach the melt with a minimum amount of water in a Telfon beaker, and rinse the crucible with a little hydrochloric acid to dissolve any adhering precipitate. Add 10 to 15 ml each of concentrated hydrochloric and hydrobromic acid and 25 ml of 72 % perchloric acid and evaporate to fumes to perchloric acid to remove the tin, arsenic, and antimony. Cool slightly and rinse down the sides of the beaker with water. Add another 10 to 15 ml of hydrochloric and hydrobromic acid plus 10 ml of concentrated hydrofluoric acid (to remove silica) and again evaporate to fumes of perchloric acid. Repeat the treatment with the above acids to ensure the complete removal of the tin, arsenic, antimony, silica, and fluoride.

2. Extraction of Interfering Elements and Titration of Aluminum

Dilute the solution to 100 ml with water, add 5 ml of glacial acetic acid and 15 ml of 25 % sodium acetate solution, and adjust the pH to 2 with hydrochloric acid or sodium hydroxide solution. Extract the interfering elements (Pb, Zn, Cu, Mn, Fe, Ag, In, Bi, W, etc.) with DEDTC and chloroform until the chloroform layer becomes colourless. If more than 3 extractions are

required to remove the interfering elements, adjust the solution to pH 2 before extraction. Titrate the aluminum by the method described for the analysis of ilmenite ores and slags (Reference 1, page 9).

The use of a mercury cathode electrolysis of the perchloric acid solution of the sample was investigated for the removal of Fe, Cu, Pb, Zn, etc., after prior removal of the Sn, As, Sb, SiO<sub>2</sub> and F and before the DEDTC extraction. During electrolysis a gray colloidal suspension was produced that so interfered with extraction that its removal more than offset the advantages of the mercury cathode electrolysis. Accordingly, an ammonium hydroxide precipitation was made to separate the aluminum (and other precipitable elements remaining in the electrolyte) from the sodium salts, the precipitate was filtered off, the paper and precipitate treated with nitric and perchloric acids to destroy the paper, and the solution was extracted with DEDTC and chloroform in the usual way. The aluminum was finally determined by titration with DCYTA as described in the recommended method.

The results obtained in these preliminary tests as well as those obtained by following the recommended procedure are given in Table 5.

The results shown in Table 5 indicate that excellent precision can be obtained on duplicate samples of these highly complex ores. Moreover, despite the problems associated with the procedure in which a mercury cathode electrolysis was used, the results were surprisingly precise. However, because of the

difficulties observed and the fact that it takes longer to complete, this procedure was abandoned in favour of the direct extraction method. Other separation steps employing precipitation, with ammonia, ion exchange, or homogeneous precipitation, for example, were not considered feasible, either because of incomplete separation of the aluminum from elements such as iron, lead, copper and zinc or because they were too time-consuming. Although it was necessary to readjust the pH of the solution to 2 frequently, no undue difficulty arose and the extraction proceeded smoothly.

The important rule to observe in the extraction step is to maintain the pH between 2 and 3 in order to avoid an emulsion or honeycomb effect and to prevent precipitation of the aluminum.

TABLE 5  
DETERMINATION OF ALUMINUM IN TIN ORES

| Sample No. | Description             | Procedure Used | % Al Found               |
|------------|-------------------------|----------------|--------------------------|
| EMP - 4541 | As Conc. N.B. Tin Ore   | 1*             | 3.17, 3.16               |
| EMP - 4542 | Cu Conc. N.B. Tin Ore   | 1*             | 1.37, 1.35               |
| EMP - 4470 | Bulk Conc. N.B. Tin Ore | 2**            | 6.41, 6.40               |
| EMP - 4471 | Ore                     | 2**            | 3.59, 3.60<br>3.59, 3.60 |

\* Preliminary tests in which a mercury cathode electrolysis was employed

\*\* The recommended procedure employing a direct extraction step.

The only value by which to judge the accuracy of the procedure was a provisional one of 3.63 % Al<sup>(2)</sup>, for the sample EMP-4471 which is in close agreement with the value obtained by the proposed procedure. The provisional value was obtained after multi-acid and fusion treatment of the samples followed by a mercury cathode electrolysis and finally precipitation of the aluminum with ammonium hydroxide and ignition to Al<sub>2</sub>O<sub>3</sub><sup>(3)</sup>.

The extraction procedure that is described in this report is easy and eminently suitable for the complete removal of a wide range of interfering elements and the subsequent titration with DCYTA can be readily made without recourse to further treatment. Therefore extraction is preferable to mercury cathode electrolysis, ion exchange, or precipitation methods for the removal of interferers.

#### D. The Determination of Aluminum in Various Minerals

As part of an investigation in our laboratories on the determination of aluminum in various minerals by atomic absorption and flame emission spectrophotometry<sup>(4)</sup>, aluminum was also determined on these same minerals by the solvent extraction - DCYTA titration method, for comparison with the instrumental values.

Calcium and magnesium were shown to interfere in the titration of aluminum in the previous work on titaniferous ores and slags if more than 20 mg of either element was present. Because large amounts of these elements, as well as silica and some fluoride were present in these minerals, the method was modified slightly to eliminate the interference of these elements.

1. Decomposition of Sample and Removal of Silica

Transfer an accurately weighed 1 to 2.5-g sample of the mineral to a platinum dish, add 10 ml of 72 % perchloric acid and 15 ml of concentrated hydrofluoric acid and evaporate to fumes of perchloric acid to volatilize the silica. Add more hydrofluoric acid and evaporate again to fumes of perchloric acid to ensure the removal of silica and fluoride. Repeat this treatment if necessary to completely decompose the sample. Finally evaporate the solution to dryness to decompose the fluoride salts and ignite the residue at low heat over a burner for a few minutes. Cool, add 10 ml of 12 M hydrochloric acid plus 20 to 30 ml of water and boil to dissolve the residual salts\*. Transfer the solution to a 200-ml volumetric flask, dilute to the mark with water, and mix thoroughly.

2. Separation of Aluminum from Calcium and Magnesium

Transfer an aliquot of the sample solution, containing 10 to 20 mg of aluminum, to a 250-ml beaker\*\*. Dilute the solution to about 100 ml with water and bring almost to a boil. Carefully add concentrated ammonium hydroxide, with stirring, until the iron just begins to precipitate and continue to add

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\* At this stage, very little insoluble residue remains, but if the amount is significant it can be filtered off, ignited, fused with a small amount of sodium carbonate, and the melt can be combined with the original filtrate.

\*\*If very little iron is present, i.e., as indicated by the absence of a strong yellow colour in the hydrochloric acid solution, add about 10 ml of a dilute hydrochloric acid solution containing 40 to 50 mg of  $Fe^{+3}$  as a carrier for the aluminum.

the ammonium hydroxide dropwise until the pH is 6.0 to 6.5 as determined by suitable pH test paper. Bring the solution to a gentle boil and boil a few minutes to coagulate the precipitate. Remove from the heat, let the precipitate settle for a minute or two, and filter through Whatman No. 40 paper. Wash the beaker and precipitate 3 times with hot 5 % ammonium chloride solution that has previously been adjusted to the methyl red end-point with dilute hydrochloric acid, or ammonium hydroxide, and discard the filtrate. Dissolve the precipitate off the paper, using hot 6 M hydrochloric acid and hot water alternately, and collect the solution in a 250-ml beaker\*.

### 3. Extraction of Interfering Elements and Titration of Aluminum

Extract the interfering elements and titrate the aluminum according to the method proposed for titaniferous ores and slags as described in the previous report in the series (Reference 1, page 8).

#### Analysis of Mineral Samples

A number of minerals were analyzed by the above procedure and the analytical results are shown in Table 6.

The results in Table 6 show that aluminum can be determined very precisely in a wide variety of minerals by the proposed extraction - DCYTA titration method. The results are in good agreement with the results obtained by atomic absorption and flame emission spectrophotometry, which, however, are less precise. The proposed method, because of its greater accuracy and precision

\*An alternative method is to treat the precipitate and paper with nitric and perchloric acids and evaporate to fumes of perchloric acid to destroy the paper.

TABLE 6

## DETERMINATION OF ALUMINUM IN VARIOUS MINERALS

| Sample No. | Sample Description     | % Aluminum Found   |                 |                    |
|------------|------------------------|--------------------|-----------------|--------------------|
|            |                        | Atomic Absorption* | Flame Emission* | Titrimetric Method |
| 1418       | Amphibole (Hornblende) | 4.52               | 4.48            | 4.76, 4.72         |
| 1419       | Biotite                | 5.71               | 5.76            | 5.48, 5.49         |
| 1422       | Labradorite (Feldspar) | 14.1               | 14.1            | 14.36, 14.33       |
| 1423       | Oligoclase             | 11.6               | 11.6            | 11.73, 11.70       |
| 1424       | Albite (Feldspar)      | 10.5               | 10.7            | 10.81, 10.77       |
| 1425       | Microcline (Feldspar)  | 9.95               | 10.0            | 9.71, 9.75, 9.72   |
| 1426       | Muscovite              | 16.2               | 16.0            | 15.84, 15.88       |

\* Reference 4



thus serves as a means of checking and evaluating the accuracy and precision of the instrumental techniques.

E. The Determination of Aluminum in Manganese Ores and Slags

As part of a research program on smelting a manganese ore in an electric furnace, many widely different synthetic manganese slags were prepared as standard reference samples for rapid analysis by X-ray fluorescence<sup>(5)</sup>. The major slag components (Table 7) include, besides aluminum, manganese, iron, calcium, magnesium, silica, and barium. The synthetic slags had to be analyzed with a high degree of accuracy and precision by an independent method not only because they were to serve as standards for the calibration of the X-ray instrument but to ascertain the effect of matrix composition on the X-ray results.

Manganese ores differ in composition from the slags mainly in the relative amounts of these elements. Because the manganese ores and slags were not as complex as the other ores, the sodium hydroxide precipitation steps were eliminated.

In the previous interference study (Reference 1, Table 7) it was found that small amounts (10 mg) of manganese could be readily extracted by DEDTC and chloroform. This known, the extraction of large amounts (50 to 500 mg) was investigated. In addition, several procedures were investigated for dissolving manganese ores and slags to see which were best applicable to the determination of aluminum.

TABLE 7

Composition of Synthetic Ferromanganese Slags\*

| Sample | MnO (a) | FeO (b) | BaO (c) | MgO (c) | CaO (c) | SiO <sub>2</sub> (d) | Al <sub>2</sub> O <sub>3</sub> (e) |
|--------|---------|---------|---------|---------|---------|----------------------|------------------------------------|
| 3425   | 32.02%  | 4.84%   | 2.12%   | 1.02%   | 0.83%   | 32.0%                | 25.59%                             |
| 3428   | 43.38   | 1.13    | 1.01    | 1.07    | 2.49    | 28.7                 | 18.82                              |
| 3429   | 39.38   | 2.05    | 1.03    | 1.08    | 0.85    | 28.5                 | 24.41                              |
| 3431   | 32.54   | 3.20    | 2.08    | 3.08    | 4.11    | 23.2                 | 28.44                              |
| 57     | 45.57   | 0.30    | 0.89    | 0.50    | 2.46    | 24.6                 | 25.26                              |
| 58     | 43.13   | 0.54    | 0.59    | 0.48    | 1.97    | 31.5                 | 20.76                              |
| 59     | 42.35   | 0.72    | 0.42    | 0.60    | 1.50    | 31.7                 | 21.56                              |
| 60     | 47.51   | 0.63    | 0.94    | 0.88    | 1.61    | 20.9                 | 26.77                              |

\*Determined by staff of Extraction Metallurgy Division, Chemical Analysis Section.

- (a) Volumetric titration
- (b) Colorimetric
- (c) Atomic Absorption sepectrophotometry
- (d) Gravimetric
- (e) By method described in this report.

Composition of Standard Manganese Ore B.C.S. No. 176\*\*

|                  | <u>Certified Value</u> | <u>Range</u>   |
|------------------|------------------------|----------------|
| Mn               | 51.3%                  | 51.04 - 51.61% |
| Fe               | 1.31%                  | 1.08 - 1.56%   |
| SiO <sub>2</sub> | 6.46%                  | 6.24 - 6.75%   |
| P                | 0.222%                 | 0.201- 0.24%   |

\*\* From certificate of analysis

Approximate Analysis

|                                |                 |                  |       |
|--------------------------------|-----------------|------------------|-------|
| MnO <sub>2</sub>               | 77.9%           | MgO              | 0.70% |
| MnO                            | 2.40            | SiO <sub>2</sub> | 6.75  |
| Fe <sub>2</sub> O <sub>3</sub> | 1.95            | SO <sub>3</sub>  | 0.03  |
| Fe (met)                       | 0.08            | TiO <sub>2</sub> | 0.02  |
| Al <sub>2</sub> O <sub>3</sub> | 1.21 (0.64% Al) | CuO              | 0.03  |
| Cr <sub>2</sub> O <sub>7</sub> | 1.29            | NiO              | 0.09  |
| BaO                            | 1.19            | CO <sub>2</sub>  | 0.30  |
| CaO                            | 0.78            | H <sub>2</sub> O | 5.00  |
|                                |                 | ?                | 0.54  |

Recommended Procedure Using Sodium Carbonate - Borax Fusion

Fuse 0.1 to 0.2 gram of manganese slag or 0.5 gram of manganese ore with a mixture of 4 grams of sodium carbonate and 2 grams of fused borax (or 4 grams of borax decahydrate) in a platinum crucible. Leach the melt with 100 ml of hot dilute (10%) hydrochloric acid in a glass beaker until the sample is completely dissolved. Add a few drops of 30% hydrogen peroxide occasionally to hasten the dissolution. Cool to room temperature, add 0.2 to 0.3 ml of 30% hydrogen peroxide, dilute the solution to about 100 ml with water if necessary, add 5 ml of glacial acetic acid and 15 ml of 25% sodium acetate solution and adjust the pH to 2 with hydrochloric acid, or sodium hydroxide, solution.

Transfer the solution to a separatory funnel and extract the solution with DEDTC and chloroform at pH 2 until the chloroform layer is colourless. If more than 3 or 4 extractions are required to remove all the interfering elements, readjust the pH to 2 before continuing with the extraction. Determine the aluminum with standard 0.02 M DCYTA solution and standard zinc solution at pH 5.5 with xylenol orange indicator (Reference 1, page 8). Run a blank determination on the reagents carried through the extraction step and correct the results if necessary.

PRELIMINARY INVESTIGATIONS

1. Determination of Aluminum after Removal of Iron and Manganese by Extraction with DEDTC and Chloroform

Experiments were done on synthetic solutions containing various amounts of iron, manganese, and aluminum which might be found in manganese ores and slags to determine if the interfering

elements could be extracted before titrating aluminum. In some of these tests, extra iron was added to simulate iron from fusing the samples with sodium peroxide in iron crucibles.

A solution containing the iron, manganese, and aluminum was diluted to 100 ml with water, 5 ml of glacial acetic acid and 15 ml of 25 % sodium acetate solution was added, and the solution was adjusted to pH 2 with hydrochloric acid, or sodium hydroxide. The solution was transferred to a separatory funnel and the iron and manganese was extracted with DEDTC and chloroform as described in the method for the titaniferous ores and slags (Reference 1, page 8). The aluminum was subsequently titrated with standard 0.02 M DCYTA and 0.02 M zinc chloride solution in the same manner also as described for the titaniferous ores and slags. The results of these tests are shown in Table 8.

Because the large amounts of manganese present required much DEDTC, chloroform, and time, more experiments were done on synthetic solutions, treated with ammonium hydroxide to separate the iron and aluminum from most of the manganese. In these tests, ammonium hydroxide was added until the solution reached pH 6 to 7, as determined by pH test paper. The solution was boiled for a short time (~ ½ minute) and then filtered. The paper and precipitate was washed twice with a hot 2 % ammonium chloride solution that had previously been adjusted to the methyl red end-point with ammonium hydroxide. The paper and precipitate was then transferred back to the original beaker in which the precipitation had been made and treated with 20 ml of concentrated nitric acid and 2 to 5 ml of 72 % perchloric acid. The solution was carefully

TABLE 8

RECOVERY OF ALUMINUM FROM SYNTHETIC SOLUTIONS AFTER  
EXTRACTION OF IRON AND MANGANESE

| Test No. | Mg of Element Present |     |       | mg Al Found                |  |
|----------|-----------------------|-----|-------|----------------------------|--|
|          | Fe                    | Mn  | Al    | After Direct<br>Extraction | After NH <sub>4</sub> OH Ppt'n<br>and Extraction |
| 1        | 10                    | 50  | 10.08 | 10.01                      | 10.14  |
| 2        | 10                    | 50  | 20.08 | 20.14                      | 20.04  |
| 3        | 10                    | 250 | 10.08 | 10.01                      | 10.01  |
| 4        | 10                    | 250 | 20.08 | 20.12                      | 19.86  |
| 5        | 200                   | 250 | 10.08 | 10.19                      | 10.13  |
| 6        | 200                   | 250 | 20.08 | 20.06                      | 20.08  |

evaporated to fumes of perchloric acid to destroy the paper. The solution was then diluted to 100 ml, 5 ml of glacial acetic acid and 15 ml of 25 % sodium acetate solution were added, and the solution adjusted to pH 2 with hydrochloric acid, or sodium hydroxide. After removing the manganese and iron by extraction with DEDTC and chloroform, the aluminum was titrated with standard 0.02 M DCYTA and standard 0.02 M zinc chloride solution. The results of these tests are also given in Table 8.

The results show that aluminum can be determined accurately and precisely after removal of the iron and manganese by extraction with DEDTC and chloroform.

The removal of small amounts of iron and manganese either by direct extraction or by extraction after an ammonium hydroxide precipitation step is relatively rapid, requiring only 3 to 4 extractions and consuming less than 25 ml of DEDTC solution and 100 ml of chloroform. Therefore, for the analysis of manganese slags in which the manganese:aluminum ratio is less than 5:1, the direct extraction procedure appears to be feasible.

The removal of large amounts of iron and manganese, however, by direct extraction required up to 20 extraction and about 100 to 150 ml of DEDTC solution and 500 to 600 ml of chloroform for each sample. If a preliminary ammonium hydroxide precipitation was made to remove the manganese less than 6 extractions were required. Nevertheless, two precipitations with ammonium hydroxide were necessary in Tests 5 and 6 because it was evident that a considerable amount of manganese had co-precipitated with the iron in the first precipitation.

In spite of this double precipitation, 30 to 40 ml of DEDTC solution and 250 to 300 ml of chloroform was required to completely remove the iron and remaining manganese. The over-all time to complete the analysis, using this procedure, was little less than with the direct extraction procedure because of the time required to precipitate and filter the aluminum and iron hydroxides and to destroy the filter paper with nitric and perchloric acids.

In none of these tests could large additions of the DEDTC be made because the dark colour of the aqueous and chloroform layers made it difficult to observe the phase interface when draining the chloroform layer; therefore, additions of the DEDTC solution were restricted to about 5 ml for each extraction. If the aqueous layer was still dark-coloured after the chloroform had settled, it could be cleared up by adding more chloroform and shaking. However, after every third or fourth addition of the DEDTC solution the pH of the aqueous solution had risen to 3.5 to 4 and the pH had to be readjusted to 2. This was necessary because of the previously noted honeycomb effect in the chloroform layer and the precipitation of aluminum.

If much manganese and iron are present, the large number of extractions required and the necessity for frequent readjustments of the pH therefore makes the direct extraction procedure too slow. On the other hand, no time is gained by the ammonium hydroxide separation step before extracting iron and the remaining manganese. Nevertheless, in spite of these difficulties, the procedure is feasible, and the results for aluminum are accurate.

## 2. Analysis of Manganese Ores and Slags

In the proceeding section, it was shown that aluminum can be determined accurately after extracting the iron and manganese, either directly or following a preliminary ammonium hydroxide separation to remove most of the manganese.

Experiments, in which both the direct extraction and preliminary ammonium hydroxide separation methods were used, were tried on manganese ores and slags. Because no standard samples of manganese ores or slags having a certified aluminum value were available, a "spiking" technique was used with some samples to establish the recovery of aluminum. The synthetic slags prepared for use in calibrating the X-ray fluorescence instrument were carefully prepared from mixtures of the pure metallic oxides and then fused in a furnace. The aluminum contents of these synthetic slags were therefore expected to be close to the actual contents and they served to check the accuracy of the proposed method.

During this work, a number of dissolution procedures were investigated to determine which of them would be suitable for the subsequent determination of aluminum. The following procedures were explored:

1. treatment with perchloric and hydrofluoric acids;
2. sodium peroxide fusion in iron crucibles; and
3. sodium carbonate + borax fusion in platinum crucibles.

After dissolution of the sample by any of the above methods, the interferers were removed either by (1) a direct extraction with DEDTC and chloroform or by (2) an ammonium hydroxide precipit-



ation to remove most of the manganese followed by extraction with DEDTC and chloroform to remove the iron and remaining manganese, etc., and the aluminum was determined. The details of these procedures are outlined below and the results are shown in Tables 9, 10 and 11.

Procedure A: Treatment with Perchloric Acid and Hydrofluoric Acid

A 0.1-gram sample of slag was treated with 10 to 15 ml of 72 % perchloric acid and 5 to 10 ml of 48 % hydrofluoric acid in a Teflon beaker and evaporated to fumes of perchloric acid several times to remove the silica and the hydrofluoric acid. The aluminum was determined by titration with standard DCYTA after removal of the impurities by extraction with DEDTC and chloroform as described in the procedure for titaniferous ores and slags (Reference 1, page 8). The results are given in Table 9.

Procedure B:

Some slag samples were dissolved by treatment with perchloric acid and hydrofluoric acid as described in Dissolution Procedure A. An ammonium hydroxide precipitation of the aluminum (plus iron) was then made to remove the bulk of the manganese. The precipitate was redissolved and the remaining iron and manganese was extracted with DEDTC and chloroform. The aluminum was finally determined by titration with standard DCYTA in the usual way. The results are given in Table 9.

Procedure C: Sodium Peroxide Fusion in Iron Crucibles

A 0.1-gram sample of slag or 0.2 to 0.5-gram samples of ore was fused with 10 times its weight of sodium peroxide in an iron crucible. After complete disintegration of the sample

TABLE 9

THE DETERMINATION OF ALUMINUM IN MANGANESE SLAGS: A COMPARISON OF RESULTS  
OBTAINED AFTER EMPLOYING VARIOUS DISSOLUTION PROCEDURES

| Sample No. | Nominal Value<br>% Al | % Aluminum Found |              |              |               |              |
|------------|-----------------------|------------------|--------------|--------------|---------------|--------------|
|            |                       | Procedure A      | Procedure B  | Procedure C  | Procedure D** | Procedure E  |
| 2930       | 10.4*                 | 9.93             | 9.77         |              |               |              |
| 2931       | 10.3*                 | 9.86             | 9.79         |              |               |              |
| 3425       | 13.2                  | 13.52, 13.57     | 13.54, 13.52 |              |               |              |
| 3428       | 9.6                   | 9.88             | 9.96, 10.10  |              |               |              |
| 3429       | 12.7                  | 13.14            | 12.92, 13.09 |              |               |              |
| 3431       | 14.8                  | 15.14            | 15.06, 15.11 |              |               |              |
| 57         | 12.7                  | 13.32, 13.37     |              | 13.43, 13.16 | 13.21, 13.11  | 13.21, 13.15 |
| 58         | 10.6                  | 10.89, 10.95     |              | 10.95, 11.03 | 10.76, 10.76  | 10.97, 10.88 |
| 59         | 11.1                  | 11.43            |              | 11.38        | 11.58         |              |
| 60         | 13.8                  |                  |              | 14.18, 14.15 | 14.20         |              |

\* Gravimetric Values

\*\* Recommended Procedure

the crucible was cooled, the fused melt was leached with water and hydrochloric acid added to dissolve the residue. After dilution to 100 ml with water, the slag samples were extracted directly with DEDTC and chloroform and the aluminum determined is described in the method for titaniferous ores and slags (Reference 1, page 8). The results are given in Table 9. The ore was treated in a similar manner but, in addition, some samples were "spiked" with known amounts of aluminum to establish that recovery of aluminum was complete (see Table 10).

TABLE 10

Recovery of Aluminum from Manganese Ore Sample  
Fused with Sodium Peroxide (Procedure C)

| Sample     | Al Added | Total Al Present | Total Al Found |
|------------|----------|------------------|----------------|
| B.C.S. 176 | none     | -                | 4.60 mg        |
| 0.5 gram   | none     | -                | 4.60 mg        |
| B.C.S. 176 | 10.08 mg | 11.92 mg         | 11.87 mg       |
| 0.2 gram   | 20.08 mg | 21.92 mg         | 21.83 mg       |

Procedure D: Fusion with Sodium Carbonate and Borax Mixture

Because of the various difficulties (removal of fluoride, incomplete dissolution of the sample, the introduction of large amounts of iron, etc.) in the preceding dissolution procedures, the sodium carbonate-borax flux fusion of the samples was explored. The procedure finally adopted is that described on page 21. A number of slag samples were analyzed by this procedure and the results are shown in Table 9. Some of the samples were "spiked"

with known amounts of aluminum to establish that recovery of the aluminum was complete, and these results are shown in Table 11.

TABLE 11

Recovery of Aluminum from Manganese Ore and Slag  
Samples Fused with Sodium Carbonate and Borax  
(Procedure D)

| Sample                     | mg Al Added    | mg Al Found*   |                | % Al Recovery |
|----------------------------|----------------|----------------|----------------|---------------|
|                            |                | "Spiked"       | "Unspiked"     |               |
| B.C.S. 176 ore<br>0.5 gram | none           | -              | 4.60, 4.60     |               |
| B.C.S. 176 ore<br>0.5 gram | 10.08<br>20.08 | 14.57<br>24.72 |                | 98.9<br>100.2 |
| 59 slag                    | none<br>10.08  |                | 11.58<br>21.37 | 98.9          |
| 60 slag                    | none<br>10.08  |                | 14.20<br>24.38 | 100.4         |
| Blank**                    | none           |                | 0.45           |               |
| Blank**                    | 10.08          | 10.50          |                | 99.7          |

\* After correcting for the blank

\*\*Blank consisted of 4 grams of sodium carbonate and 2 grams of borax.

Procedure E:

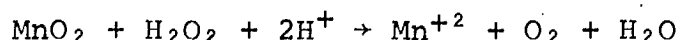
Some slag samples were dissolved by Dissolution Procedure D, and an ammonium hydroxide precipitation of the aluminum and iron was made to remove the bulk of the manganese. The precipitate was redissolved and the remaining iron and manganese were extracted with DEDTC and chloroform. The aluminum was finally determined by titration with standard DCYTA; see Table 9.

These results show that the values for aluminum, obtained by the recommended method (Procedure D), agree well with those obtained by the other procedures. Rapid and complete decomposition of either ores or slags is obtained by the sodium carbonate-borax fusion. Dissolution of the fused sample in dilute hydrochloric acid gives a clear solution with only an insignificant trace of unattacked material.

A comparison of the results of Procedure D with the results of Procedure E shows that a preliminary ammonium hydroxide step is unnecessary to remove the bulk of the manganese and a direct extraction of the interfering elements may be used instead. The use of a sodium carbonate-borax flux has the additional advantage that it introduces no iron and, if an ammonium hydroxide separation step is required (in the event that large amounts of calcium and magnesium are present), there is less co-precipitation of manganese with the iron. For those samples in which an ammonium hydroxide separation was made, a single precipitation was sufficient to remove the bulk of the manganese and only 3 or 4 extractions with DEDTC and chloroform were then required to completely remove all interferers.

The nominal values for aluminum in the synthetic manganese slags used in the tests are those which were calculated from the weight of pure  $Al_2O_3$  used in the preparation of the slags. The slightly higher percentage of aluminum as determined in the samples by the proposed method is attributed to the fact that the samples were fused in a furnace after mixing and a slight loss in weight took place.

The addition of hydrogen peroxide in the extraction step has a remarkably beneficial effect that enables the manganese to be extracted readily, shortens the extraction time considerably, and in most cases eliminates a preliminary ammonium hydroxide separation. Normally, with several metals that have different oxidation states, the formation of dithiocarbamate complexes is accompanied by redox reactions and manganese (II), for example, is oxidized to manganese (III) or even to manganese (IV)<sup>(6)</sup>. On the other hand, in acid solution, higher valences of manganese are prevented by the reducing action of hydrogen peroxide<sup>(7)</sup>,



Thus, it appears that the presence of hydrogen peroxide prevents the oxidation of Mn (II) to a higher-valence by the DEDTC and this accounts for the fact that less DEDTC is consumed in the extraction step than if the peroxide were absent. The manganese dithiocarbamate complex that is formed is much more readily extracted by chloroform.

Care must be taken not to add too much peroxide to the acid solution lest DEDTC be decomposed. In the titrations of aluminum which followed, a slight fading of the indicator may have been due to the peroxide or to organic decomposition products left in solution. However, the end-point was still clearly visible, and a few more drops of xylenol orange indicator overcame the fading.

Table 11 confirms the complete recovery of aluminum from ore and slag samples that were "spiked" with known amounts of aluminum and shows that the presence of borax has no adverse

effect in either the extraction step or the titration of aluminum. In other tests, it was established that no aluminum was contained in the sodium carbonate and the blank was due entirely to the borax. The blank obtained on an unextracted 2-gram portion of the borax was equivalent to 0.48 mg of Al but, on an extracted portion, it amounted to 0.45 mg of Al (the true Al content or 0.02 % Al). Extraction of the borax with DEDTC and chloroform resulted in a dark brown extract, the colour presumably due to traces of iron; this probably accounts for the slight difference between the values for the extracted and unextracted blanks. With other lots of reagents, however, the differences could be much greater, therefore, blanks should be determined on reagents that are carried through the extraction step. In any case, it is better to obtain supplies of aluminum-free reagents if at all possible.

A comparison of the results obtained by the recommended method (Procedure D) with those obtained by either Procedure A or Procedure C shows that large amounts of silica can be tolerated without difficulty. In procedure A, the silica is removed by treatment with hydrofluoric acid whereas in either Procedure C (sodium peroxide fusion) or Procedure D (borax-sodium carbonate fusion) the silica is not removed.

The gravimetric results for Samples 2930 and 2931 are significantly higher than the titrimetric results obtained by Procedures A and B. This was expected because the  $Al_2O_3$  residue was visibly contaminated with impurities (Fe, Mn, etc.) and the gravimetric values were not corrected for them. The values

determined by the extraction-titrimetric method are, therefore, believed to be more reliable.

The results obtained by Procedures A and B agree closely with each other but it was found in other tests that a slight residue sometimes remained undissolved after treatment of the samples by Procedure A and that erratic and/or lower results were obtained. Moreover, difficulties were encountered in detecting the end-point in the titration of aluminum. On the other hand, using Procedure B, any residue was recovered in the ammonium hydroxide precipitate which, along with the filter paper, was readily dissolved by nitric and perchloric acids.

The main disadvantages of either Procedure A or Procedure B, besides having to remove fluoride completely, were that a large amount of manganese was difficult to remove, that excessive amounts of DEDTC and chloroform were needed in the extraction step, that frequent adjustment of the pH of the solution was necessary, and that, consequently, extraction was slow; see pages 24 and 25.

Table 9 shows that reproducible results can be obtained on samples that are fused with sodium peroxide and extracted directly with DEDTC and chloroform (Procedure C). The results agree closely with those obtained by the other procedures. The sodium peroxide fusion gave complete solution of all the slag samples and no difficulty was observed in the subsequent titration of the aluminum. Again, the manganese was difficult to remove and the same extraction problems were noted as for Procedure A.



Table 10 confirms the complete recovery of aluminum from samples of a manganese ore "spiked" with known amounts of aluminum. The same difficulties were experienced in extracting manganese as were experienced with the slag samples, however, good recoveries of the aluminum were obtained.

The extraction of manganese was slower than that of iron. For example, in spite of the large amount of iron that was introduced from the iron crucibles, it was readily extracted and appeared to be removed in the first few extractions. Manganese, on the other hand, continued to be extracted long after the iron had been removed. The addition of hydrogen peroxide in the extraction step (as recommended in the sodium carbonate-borax fusion procedure) after dissolution of the samples by either A or C procedure would likely avoid this difficulty but was not reinvestigated because the borax fusion was simpler and it avoided having to introduce either hydrofluoric acid or iron.

The fusion of the sample with sodium peroxide in nickel or zirconium crucibles was not considered feasible because this would introduce either nickel or zirconium which would complicate the procedure more than would introducing iron.

Barium, which is present in the slags in amounts up to 2 % as BaO, is not extracted by DEDTC and chloroform, so tests were done to determine if it interfered in the titration procedure. It was found that up to 300 mg of barium had no significant effect on the results. Calcium and magnesium were also possible interferers<sup>(1)</sup>, but no difficulty was expected with the amounts present in the slags and none was in fact observed. In the

event that an ore, or slag, contained large amounts of calcium or magnesium, these elements could be largely removed by ammonium hydroxide precipitation.

#### SUMMARY

It has been shown that aluminum can be determined accurately and precisely in a large variety of minerals, ores and slags by a titrimetric procedure using DCYTA and xylenol orange indicator. Procedures are described for the decomposition and dissolution of the samples and for the removal of various interfering elements prior to the titration of aluminum. In general, many interferences can be removed simply by direct extraction with sodium diethyldithiocarbamate and chloroform but some ores and minerals, because of their complexity, require treatment to either volatilize or precipitate specific interferences such as fluoride, tin, rare earths before the extraction is made to remove the remaining interferers.

The procedure has been applied to the determination of aluminum in ilmenite ores and slags, chromite, coke, fly ash, uranium ores, tin, ores, manganese ores and slags, and various minerals. The method is less time-consuming and more accurate than the gravimetric method in which the aluminum is separated as the hydrous aluminum oxide and ignited to aluminum oxide. It serves as a versatile method for the determination of aluminum in samples that are to be used as reference standards to calibrate instrumental methods such as atomic-absorption and X-ray fluorescence spectrometry.

#### ACKNOWLEDGEMENTS

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